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Preparation of aluminum doped zinc oxide films by sol-gel method : thermoelectric power and Hall voltage measurements

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Abstract : Transparent and conducting aluminum doped zinc oxide (ZnO) films were prepared by the sol-gel technique on silica-glass substrates. A simple analog subtraction circuit has been fabricated to measure the Seebeck coefficient of a specimen containing 1.7 at% Al at room temperature under high vacuum. This is small and negative. X-ray diffractogram indicates that the film is polycrystalline and scanning electron microscopy affirms the polycrystallinity with a grain size of approximately 40 nm. The Hall voltage at room temperature is also found negative. An attempt has also been made to explain the two experimental data.

Keywords : Sol-gel, thermoelectric power, Hall voltage

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1. Introduction

ZnO thin films are technologically important due to their range of electrical and optical properties, which make them suitable for a variety of applications, such as solar cell electronics, gas sensors and optical wave-guide devices *etc.* A wide variety of coating techniques for the transparent thin film are known. Sol-gel [1] method is another attractive technique for obtaining thin films and has the advantages of easy control of the film composition and easy fabrication of a large area film with low cost. There are very few data on the thermoelectric power and Hall voltage of the ZnO film prepared by sol-gel technique. We report here the thermoelectric power, electrical resistivity and Hall voltage measurements of 1.7 at% Al doped ZnO films at room temperature. Thermoelectric power (TEP) is most sensitive quantity to any change or distortion of the Fermi surface in the material. In this experiment, we use an analog subtraction circuit to measure the TEP of the sample to a heat pulse. Hall mobility of the film has been measured by Vander Pauw point probe technique using a square configuration.

2. Preparation of films

Transparent aluminum doped zinc oxide (ZnO) films have been prepared *via* sol-gel method on silica-glass substrates. In this method zinc acetate 2 hydrate [$Zn(CH_3COO)_2$, $2H_2O$] has been first dissolved in dehydrated isopropyl alcohol (Pr^iOH). The resultant solution has been mixed thoroughly on a magnetic stirrer. We then add some solstabilizers into the solution until it becomes transparent from milky. For aluminum doping, we have mixed the reagent $Al(NO_3)$, $9H_2O$. Al/Zn ratio was kept at 1.7 at%. The solution after proper mixing has been filtered and kept for one day before deposition on the glass substrate by the drain coating method. The substrate was heated at different temperatures to crystallize the zinc oxide film. The samples were prepared by repeating the procedure ten times.

3. XRD and SEM studies

The X-ray diffraction spectra for 1.7 at% Al doped ZnO thin films prepared at one of the temperatures (550°C) shown in Figure (1) indicate that the films are polycrystalline nature. These films have a better orientation along [200] direction. The SEM micrographs of the film with 1.7 at% aluminum contents, heated at the same temperature have been shown in Figure (2). The grain size is around 40 nm for the film. The grains are regular in size and shape and densely packed with little porosity. The EDX measurement also agree with the composition quoted above.

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4. Hall voltage measurements

The electrical conductivity, the carrier concentration and Hall mobility of the film were measured at room temperature by the Van der Pauw point probe technique using a square configuration. The four contacts were gold deposited. The measurements were carried out utilizing a magnetic field of 6 Kilo-Gauss, the maximum obtainable in our instruments.

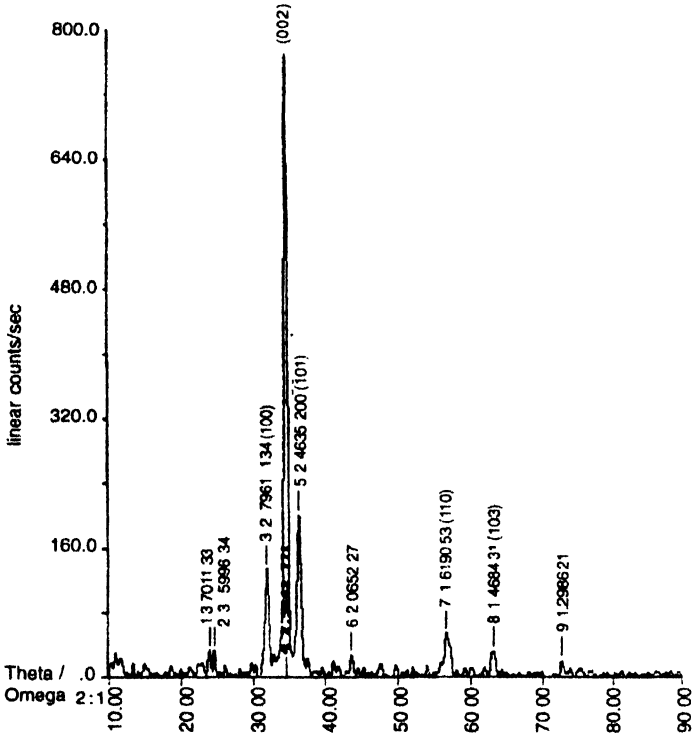

Figure 1. XRD spectra for 1.7 at% Al doped ZnO thin film.

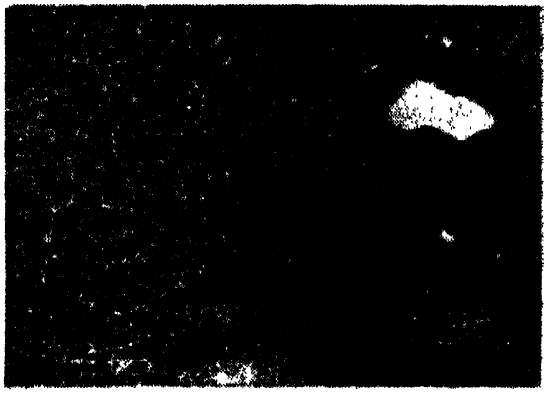

Figure 2. SEM micrograph of 1.7 at% Al doped ZnO thin film.

Several Hall voltage readings were taken changing the current and plotted in a graph. From the slope of this graph the carrier concentration (N_d) has been calculated using the following expression

$$N_d = IB / V_H e d, \tag{1}$$

where V_H = is the Hall voltage, I = applied current, (V_H/I) is the slope of the V_H *vs* I graph, B is the magentic field, e = electronic charge and d = thickness of the film.

Resistivity has been measured by interchanging the current and potential terminals as the usual practice in four probe measurements. Relevant expression for this configuration is

$$\rho = (\pi d / \ln 2)(V / I), \tag{2}$$

V = measured voltage, I = measured current,

$$1/\rho = \sigma = N_d e \mu. \tag{3}$$

Using expressions (1), (2) and (3), the mobility (μ) can be easily determined. The Hall measurement indicates that the voltage is negative. The resultant value of N_d from the slope of the graph is 1.4×10^{17} / cm^3 and mobility comes out to be 27.5 cm^2/volt-sec from eq. (3) combining corresponding resistivity data.

5. Thermoelectric power

Figure (3) identifies the primary thermoelectric voltage ΔV_I (I = 1, 2, 3) used to determine the absolute sample thermoelectric

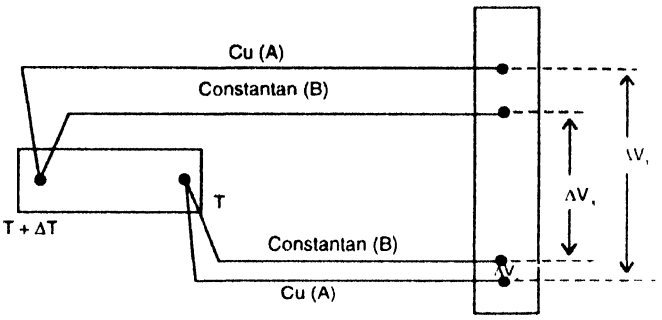

Figure 3. Schematic diagram of experimental setup for thermoelectric power measurement

power Q_S, Q_A and Q_B are the absolute thermoelectric powers of the thermocouple arms. If T is the sample temperature, T_r reference temperature, ΔV's can be defined as

$$\Delta V_1 = (Q_S - Q_A)\,\Delta T,$$

$$\Delta V_2 = \int (Q_A - Q_B)\,dT,$$

$$\Delta V_3 = (Q_S - Q_B)\,\Delta T,$$

where ΔT is the temperature difference between two thermocouple junction attached to the sample. The simplest experimental approach is to apply a heat pulse to one end of the sample, develop a small temperature difference ΔT and measure the voltages as it is or amplify them and get plotted in a computer. The ratio of ($\Delta V_1 / \Delta T$) and ($\Delta V_3 / \Delta T$) are the relative thermoelectric powers of sample and element A(Cu) and element B (constantan) respectively. In fact, we have used one analog subtraction circuit which amplifies the subtraction voltage ($\Delta V_1 - \Delta V_3$) and ΔV_1 subsequently, the plot of ΔV_1 subtraction voltage yields the thermoelectric power and store in the PC. In order to measure the absolute thermoelectric power, one of the arms used was lead (Pb) whose thermoelectric power

is almost nil. The corresponding graph is shown in Figure (4) whose slope is 0.23 mv/^{0}K.

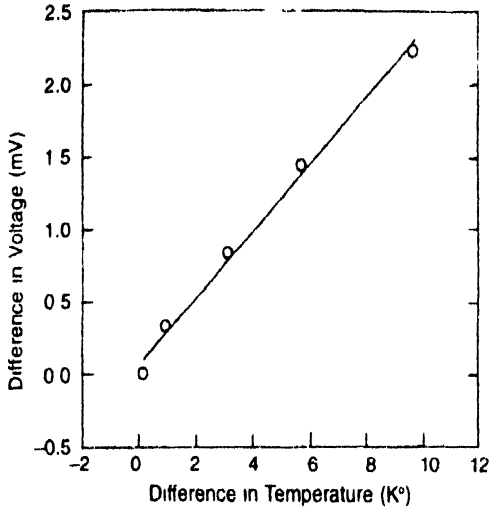

Figure 4. Differential Voltage as a function of differential temperature at room temperature

6. Discussion

As Hall measurements indicate n-type conduction the thermoelectric power should be negative. There are situations where n-type of materials show p-type thermopower [2,3]. But in this case, the thermoelectric voltage shows that the major carriers are negatively charged. Most of the existing theories concern simple semiconducting materials like Ge. In the case of extrinsic non-degenerate semiconductor, there are two contributions to thermoelectric power. One of them is the energy flux relative to electrochemical potential carried through the thermoelectric circuit and the other resulting from electron phonon interaction. Considering both contributions [4], our experimental value fits well to the theoretical value if we assume that the interaction of the electrons is with ionized impurity. Further work on this area is under progress.

References

[1] M Ohyama, H Kozuka and T Yoko *J Am Ceram Soc* **81** 1622 (1998)

[2] N F Mott and E A Davis *Electronic Progress in Non Crystalline Materials*, 2nd edn (Oxford : Clarendon) (1979)

[3] T H Geballe and G W Hull *Phys Rev* **98** 940 (1955)

[4] G C Jain, W B Berry *Transport Properties of Solids and Solid State Energy Conversion* (Bombay : Tata McGraw-Hill) (1972)